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(54) POLYSULFONE HOLLOW FIBER MEMBRANE OF SELECTIVE PERMEABLILITY

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a polysulfone hollow fiber membrane having the sharp molecular weight fractionation and to be used safely by so crosslinking a hydrophilic polymer as to be insoluble in water, making it be existent in the membrane structure in the hydrogel state and setting the dialysance of phosphoric acid in a module in a specified range.
SOLUTION: A polysulfone hollow fiber membrane is composed of a polysulfone resin containing a hydrophilic polymer, and a hydrophilic polymer is so crosslinked as to be insoluble in water, and the water is contained therein to exist it in the membrane structure in the hydrogel state, and the dialysance of phosphoric acid (0.7 m2 conversion) is so prepared as to be in the range of 136-145 ml/min. in a module. The polysulfone hollow fiber membrane of selective permeability is manufactured by adding a polysulfone resin, a hydrophilic polymer, a solvent for solving the resin and the polymer and an additive for pore diameter control such as water, and forming a uniform spinning stock solution by the publicly-known process.

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CLAIMS

[Claim(s)]
[Claim 1] It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of a phosphoric acid [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 136 or more ml/min and 145 ml/min or less further.
[Claim 2] The polysulfone system permselectivity hollow fiber according to claim 1 in which the hydrophilic macromolecule which exists in a hollow fiber is unevenly distributed near the inside front face of a hollow fiber.
[Claim 3] The polysulfone system permselectivity hollow fiber according to claim 1 or 2 to which a hollow fiber is characterized by not making parenchyma top albumin penetrate.
[Claim 4] It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of a urea [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 166 or more ml/min and 172 ml/min or less further.
[Claim 5] The polysulfone system permselectivity hollow fiber according to claim 4 in which the hydrophilic macromolecule which exists in a hollow fiber is unevenly distributed near the inside front face of a hollow fiber.
[Claim 6] The polysulfone system permselectivity hollow fiber according to claim 4 or 5 to which a hollow fiber is characterized by not making parenchyma top albumin penetrate.
[Claim 7] It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of a creatinine [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 142 or more ml/min and 149 ml/min or less further.
[Claim 8] The polysulfone system permselectivity hollow fiber according to claim 7 in which the hydrophilic macromolecule which exists in a hollow fiber is unevenly distributed near the inside front face of a hollow fiber.
[Claim 9] The polysulfone system permselectivity hollow fiber according to claim 7 or 8 to which a hollow fiber is characterized by not making parenchyma top albumin penetrate.
[Claim 10] It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of vitamin B12 [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 92 or more ml/min and 94 ml/min or less further.
[Claim 11] The polysulfone system permselectivity hollow fiber according to claim 10 in which

the hydrophilic macromolecule which exists in a hollow fiber is unevenly distributed near the inside front face of a hollow fiber.
[Claim 12] The polysulfone system permselectivity hollow fiber according to claim 10 or 11 to which a hollow fiber is characterized by not making parenchyma top albumin penetrate.
[Claim 13] It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose permeable ability of a physiological saline [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] is 403 ml/hr/mmHg - 955 ml/hr/mmHg further.
[Claim 14] The polysulfone system permselectivity hollow fiber according to claim 13 in which the hydrophilic macromolecule which exists in a hollow fiber is unevenly distributed near the inside front face of a hollow fiber.
[Claim 15] The polysulfone system permselectivity hollow fiber according to claim 13 or 14 to which a hollow fiber is characterized by not making parenchyma top albumin penetrate.

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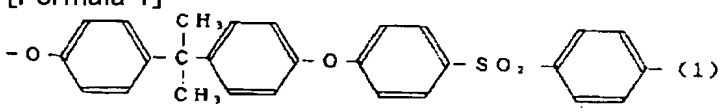
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Though a hydrophilic macromolecule is contained, a bridge is constructed, and this invention is insolubilized and relates to the high performance hollow fiber defecated by altitude.
[0002]
[Description of the Prior Art] As for the film which consists of polysulfone system resin which is a hydrophobic macromolecule, the application in each field is developed by the good mechanical property and thermal resistance until now.
[0003] However, in order to make the engine performance of the film dried by the firm water repellence which be the description of this material film in order to carry out oxyethylene gas sterilization like a certain kind of film for example, discover, it needed to be made to get used with water at the time of use, and the means of infiltrate hydrophilic matter, surfactants, etc., such as a glycerol, into the film be took. Moreover, the various approaches also as the hydrophilization approach of the film itself were examined until now, and it has been proposed about improvement in a contamination-proof student, and an improvement of a living body adaptation student.
[0004] As one approach, the attempt which is going to carry out hydrophilization of the polymer itself by chemical modification is shown as the sulfonation (JP,55-36296,A) approach by concentrated sulfuric acid. However, although the hydrophilization of a polymer can be achieved by this approach, the engine performance and quality of an actual demarcation membrane are not ****(ed), and that film production means is not clear, either.
[0005] About the blend with polysulfone and a hydrophilic giant molecule, in order to raise the spinning nature, addition spinning, such as a polyvinyl pyrrolidone and a polyethylene glycol, is examined (Journal Of Applied Polymer Science Vol.20, 2377-2394). By the still more nearly same technique, although it is the sheet-like film, the method (JP,55-106243,A) of extracting and removing a hydrophilic macromolecule after film production is also shown. moreover, JP,58-104940,A **** -- a possibility that actuation may spoil expected membraneous ability to a complicated top although the approach of carrying out bridge formation immobilization of the hydrophilic macromolecule in the film according to a cross linking agent or a physicochemical catalyst is shown -- it is -- moreover, the effectiveness -- enough -- **** -- it cannot say. Although the addition of a hydrophilic macromolecule is reduced in JP,61-93801,A and the application to a medical-application way is shown in it, perfect extract and removal of a hydrophilic macromolecule are difficult as indicated.
[0006] Furthermore, JP,61-238306,A Although the approach of carrying out bridge formation immobilization of the hydrophilic macromolecule by heat treatment or radiation treatment is shown in JP,63-97205,A and JP,63-97634,A, it has come to obtain film to which albumin is not made to leak substantially small [an aperture].
[0007] the approach of on the other hand fixing a hydrophilic macromolecule and a compound to a film front face -- JP,62-11503,A, JP,63-68646,A, and JP,62-125802,A etc. -- it is indicated. However, these approaches do not necessarily have enough hydrophilization, or the elution of

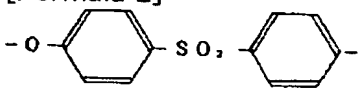
the hydrophilic compound from this film at the time of actual use is not stopped, and application in the industrial field as which medicine and advanced cleanliness are required is not achieved.
[0008]
[Problem(s) to be Solved by the Invention] This invention cancels the trouble of the conventional technique and uses as an offer plug the polysulfone system permselectivity hollow fiber which are medicine and fields, such as food stuff industry, and molecular weight fractionation with few underwater effluents is sharp, and can be used in comfort according to separation of matter especially with small molecular weight, such as separation, recovery, etc. of removal and the useful matter of an undesired substance.
[0009]
[Means for Solving the Problem] This invention has the next configuration, in order to attain the above-mentioned purpose.
"It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of a phosphoric acid [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing (1) hydrophilic-property macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 136 or more ml/min and 145 ml/min or less further.
[0010] (2) It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of a urea [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 166 or more ml/min and 172 ml/min or less further.
[0011] (3) It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of a creatinine [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 142 or more ml/min and 149 ml/min or less further.
[0012] (4) It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose dialysances (0.7m 2 conversion) of vitamin B12 [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] are 92 or more ml/min and 94 ml/min or less further.
[0013] (5) It is the polysulfone system permselectivity hollow fiber for medical dialysis modules whose permeable ability of a physiological saline [in / the bridge was constructed over this hydrophilic macromolecule in the polysulfone system hollow fiber containing a hydrophilic macromolecule, and it has insolubilized in water, and water is contained, and it exists in membrane structure in the state of a hydrogel, and / a module] is 403 ml/hr/mmHg - 955 ml/hr/mmHg further. "
[0014]
[Embodiment of the Invention] The polysulfone system permselectivity hollow fiber of this invention has the description at the place which consists of polysulfone system resin containing a hydrophilic macromolecule.
[0015] With polysulfone system resin here, it consists of a formula (1) or a formula (2). Namely,
[0016]
[Formula 1]



(1)

[0017]

[Formula 2]



(2)

[0018] Although it is resin which consists of a ********** unit, the functional group may not be included, or the radical of an alkyl system may not be included, and it is not limited especially.
[0019] After making a film production undiluted solution contain a hydrophilic macromolecule, the polysulfone system permselectivity hollow fiber which consists of this resin produces this to a hollow fiber by the well-known approach, and is manufactured. That is, after carrying out the churning dissolution of the additives, such as water, [for above-mentioned polysulfone system resin and a hydrophilic macromolecule, the solvent that dissolves them further, and aperture control] and obtaining a uniform spinning undiluted solution, this spinning undiluted solution is produced to a hollow filament by the well-known approach.
[0020] As a hydrophilic giant molecule, the giant molecule which was excellent in hydrophilic properties, such as a polyvinyl pyrrolidone (it is called Following PVP) or a polyethylene glycol, for example can be used here.
[0021] moreover, independent [, for example / in dimethyl acetamido (it is called Following DMAc), dimethyl sulfoxide (it is called Following DMSO), or N-methyl pyrrolidone] as a solvent which dissolves both polysulfone system resin and a hydrophilic giant molecule -- or it can be mixed and used.
[0022] In this case, since the molecular weight of polysulfone system resin and a hydrophilic macromolecule, concentration, the class of solvent and combination, or the amount of an additive influences greatly the engine performance and mechanical property of not only film production nature but the film, choosing carefully is desirable.
[0023] The concentration of the polysulfone system resin in the spinning undiluted solution at the time of constituting the polysulfone system permselectivity hollow fiber of this invention is good to be in 10 - 30% of the weight of the range preferably.
[0024] Though a hydrophilic macromolecule is especially included so much by this invention, since it fixes to the interior of the film firmly by the radiation-induced crosslinking reaction, it is possible sufficient hydrophilic property for the film and to give high water content. However, since permeability is also influenced by the swelling of the hydrophilic macromolecule in the film, the amount of a hydrophilic macromolecule is good to adjust so that it may be preferably contained three to 15% of the weight still more preferably one to 20% of the weight in the film. That is, the amount of the hydrophilic macromolecule in a spinning undiluted solution is 3 - 30 % of the weight preferably. If this is said at a rate of all the polymers in an undiluted solution, it will be 15 - 50 % of the weight still more preferably five to 70% of the weight preferably. moisture absorption desirable to the pan of 15 - 30 % of the weight in the case of this hollow fiber that the moisture absorption of this hollow fiber obtained in this way is 10 - 50 % of the weight preferably, and has suitable permeability especially -- being shown -- in addition -- and it has sufficient hydrophilic property.
[0025] Next, if the molecular weight of the hydrophilic macromolecule used for this invention is explained, the desorption of a hydrophilic macromolecule will become the factor which forms membranous pore one. If molecular weight becomes large, a membranous aperture will become large, and the inclination becomes strong when the freezing characteristic of the infusion enclosed especially with the interior of a hollow filament is low. Crosslinking reaction tends to progress and there is an inclination for immobilization on the film to become easy, so that molecular weight is large on the other hand. Therefore, the molecular weight is preferably good 10,000-500,000, and to use the thing of 30,000-100,000 still more preferably.
[0026] The presentation of the infusion furthermore enclosed with the interior of a hollow filament plays a big role especially in aperture control by the freezing characteristic. That is, when freezing characteristic is low, the aperture of the internal surface of a hollow fiber becomes large, water permeability becomes high and, on the other hand, protein leak produces it. Moreover, water permeability becomes low, although leak of protein is lost when freezing

characteristic is high. Therefore, it is desirable to change the presentation of infusion according to the application and the purpose of a hollow fiber.
[0027] However, although the film by this invention shows high water permeability as compared with the conventional hollow fiber, it has the description at the point that leak of protein is not accepted. This is because membranous transparency balance has been improved with the hydrophilic giant molecule centralized on the compact layer near the film internal surface (distributed partially).
[0028] Moreover, although the polysulfone system selection transparency hollow fiber of this invention has high water permeability, it demonstrates the property by the sharp molecular weight fractionation especially in a usage without blinding by protein like for example, an endotoxin removal filter. That is, even if it uses the module of a small film surface product, it has the high removal engine performance, without being accompanied by the pressure loss of a circuit, and it becomes possible to supply an endotoxin free-lancer's ******.
[0029] the bottom of the conditions to which the hollow fiber of this invention was set as mentioned above -- an annular slit mold -- from a mouthpiece, by the dryness-and-moisture type spinning method, in order to prevent the regurgitation and coagulation, and a membraneous ability change rinse and according to desiccation, after giving and rolling round desiccation inhibitors, such as a glycerol, and cutting to predetermined die length, the mounting fluid inside a hollow filament is deliquored and it usually considers as a thread.
[0030] In order to carry out radiation-induced crosslinking of this hollow fiber, the following approaches are used preferably.
[0031] the approach of carrying out radiation bridge formation processing in the state of (1) thread and (2) -- it is the approach of once carrying out a modularization and carrying out radiation-induced crosslinking processing etc. [namely,]
[0032] In this case, the quantity of radiation of a radiation required for bridge formation is 10 - 50 KGy, it has the inclination for sufficient crosslinking reaction not to be performed when lower than this, and when too high, it has the inclination for degradation of a hollow fiber to advance.
[0033] In performing bridge formation processing by the radiation in the state of a thread, in order that the adhering glycerol may check promotion of crosslinking reaction, it is desirable to carry out bridge formation processing, without lessening this coating weight as much as possible, or performing glycerol processing. In that case, radiation-induced crosslinking processing is performed to the bottom of strict adhesion liquid management so that the membranous engine performance may carry out desiccation degradation and hydrogel structure may not be destroyed. Then, a modularization is performed by the same approach as the usual thread.
[0034] A well-known means performs the approach of a modularization.
[0035] That is, although a thread is inserted in the case of styrene resin etc. and centrifugal potting is usually performed using the potting material of a polyurethane system, the case of an AS resin, polycarbonate resin, etc. may be used, or the so-called standing potting which is potting material with thermal resistance, such as an epoxy resin and silicon resin, and carries out potting of the pars basilaris ossis occipitalis where a thread is stood may be performed. Anyway, although it is desirable to perform the modularization according to the purpose and an application, what is necessary is just the material which can penetrate a radiation required for bridge formation and immobilization of the hydrophilic macromolecule which is the description of this invention etc. Then, a modular end face is cut, a hollow filament aperture is prepared, it equips with header packing etc., and a leakage test is performed.
[0036] Next, the solvent of the minute amount which remains inside a hollow fiber, the glycerol given for desiccation prevention are rinsed. In order to insolubilize by next bridge formation and immobilization about the hydrophilic macromolecule in the film at this time, it is not necessary to mind especially. However, that (it carries out more than percentage of saturatel water content) which is changed into the condition that holding the whole film to sufficient damp or wet condition was preferably filled up desirable especially with water in the module is good. Usually, the percentage of saturatel water content of this hollow fiber is just over or below

400%, and it is desirable to hold water content more than this.
[0037] Since percentage of saturatel water content is changed into the condition of it being expressed with the percentage (%) to the hollow fiber weight after drying a hollow fiber for 5 hours at 130 degrees C of the moisture content when carrying out at-long-intervals alignment dehydration by 0.5G for 1 minute, and having filled up water with the below-mentioned example, all are held to about 1000%. Since the inclination whose bridge formation water-insoluble part of a water soluble polymer it becomes impossible to fully construct a bridge in the water soluble polymer by the below-mentioned radiation, and decreases is shown, the condition of under percentage of saturatel water content takes cautions.
[0038] In this invention, after holding a module to sufficient damp or wet condition in this way, radiation irradiation, especially gamma irradiation are performed to a hydrophilic macromolecule, and bridge formation and immobilization are performed. as compared with the conventional chemical approach, the crosslinking reaction by this radiation is boiled markedly, is trustworthy and is performed to homogeneity.
[0039] At this time, degradation of polysulfone system resin, a potting material, a case, etc., etc. may be followed on bridge formation and coincidence of a hydrophilic giant molecule. Therefore, as for the amount of radiation irradiation, it is desirable to carry out in the range of 10-50 KGy preferably. Although the ductility fall of some hollow filament and coloring of a header case may be accepted by this radiation irradiation, it is not extent which becomes especially a problem.
[0040] By this radiation irradiation, this module can also be sterilized to coincidence. Although the amount of radiation irradiation in which the sterilization in this case is possible is also within the limits of 10 used by above-mentioned crosslinking reaction - 50 KGy, if in charge of actual sterilization, in this module, it is desirable to measure the D value which shows the relation between quantity of radiation and sterilization effectiveness (ratio of the number of microorganism after the exposure to the number of microorganism before an exposure), and to set up quantity of radiation.
[0041] As an above-mentioned radiation, although a gamma ray or an X-ray can be used, a gamma ray is desirable from the point of permeability, the ease of carrying out of bridge formation, etc. It is desirable to use the advantageous electron ray conversion X-ray in facility as an X-ray. However, it is desirable in the case of a conversion X-ray, to change the exposure approaches, such as thickness of an object and arrangement, since the permeability is inferior to a gamma ray.
[0042] When the approach indicated by the eluting material test (henceforth artificial-kidney criteria) of the permeable membrane of "the quality of a dialyzer and the examining method" by which the hollow fiber by which the hydrophilic macromolecule obtained in this way was constructed [the bridge] for it and fixed was shown in dialysis mold hemodialysis apparatus acknowledgement criteria estimates an effluent, the absorbance in the wavelength of 220-350nm shows the outstanding value or less of 0.1 by 10mm of layer length as an ultraviolet-absorption spectrum by it.
[0043] In making this module into clarification further, the sealing liquid containing an effluent is once discharged and it rinses this module again. And it is filled up with a physiological saline etc. water or if needed in a module. At this time, in order to heighten the sterilization effectiveness, it is also possible to add a hydrogen peroxide to restoration underwater.
[0044] An enclosure seal is performed into a polyethylene bag etc. and this module is packed up in a corrugated paper case etc. Although sterilization by radiation (gamma ray) exposure is performed in this condition, also in this case, an above-mentioned D value is measured and suitable quantity of radiation is set up. If there is too much quantity of radiation, in order to cause degradation of a film material, a case, etc. also in this case, it is desirable to irradiate suitable dosage.
[0045] As mentioned above, in order that the polysulfone system permselectivity hollow fiber of this invention may hold the outstanding engine-performance balance of not carrying out protein leak, having high water permeability, in the manufacture process, desiccation is not performed in principle.

[0046] Probably because the polysulfone system permselectivity hollow fiber of this invention is manufactured by the above approaches, it is completed in the characteristic form of a hydrogel condition. That is, the added hydrophilic macromolecule distributes on the whole film, and is being constructed [the bridge] for it and fixed in the condition of having become entangled firmly. After this is immersed in DMAc in this hollow fiber and extracts the polysulfone system polymer in the film, the hydrophilic macromolecule over which the bridge was constructed is in the condition holding a hollow filament-like gestalt, and is clear from being observed with an optical microscope.
[0047] Thus, while insolubilizing in water and decreasing the effluent from this film extremely by carrying out radiation-induced crosslinking of the hydrophilic macromolecule, it became possible by giving sufficient hydrophilic property for the film to use it as an outstanding hydrogel-like selection transparency hollow fiber of solute permeability.
[0048] drawing 1 -- the extract from the hollow fiber of an example 6 and the example 6 of a comparison -- a spectrum -- it is an ultraviolet absorption spectrum when measuring by ****** UV-160 (Shimadzu make). it turns out that the absorbance of the extract from the bridge formation hollow fiber of an example 6 is very low, namely, it is lower than a target absorbance, an effluent is markedly alike, and it decreases as compared with the absorbance of the extract from the hollow film for which a bridge is not constructed [of the example 6 of a comparison] so that clearly from the absorption spectrum of drawing 1 .
[0049] Drawing 2 is the microphotography (50 times) in which the underwater fiber configuration of the polysulfone system permselectivity hollow fiber of this invention containing bridge formation PVP was shown. As for this hollow fiber of this invention containing bridge formation PVP, it turns out like drawing 2 that the hollow filament configuration is held, without eluting PVP underwater.
[0050] Drawing 3 is a microphotography (50 times) in which the fiber configuration when dissolving the polysulfone system hollow fiber before constructing a bridge in PVP contained in a hollow filament in DMAc is shown. Drawing 3 shows that PVP as well as polysulfone was eluted and the gestalt has collapsed.
[0051] Drawing 4 is a microphotography (50 times) in which the fiber configuration when dissolving in DMAc the polysulfone system permselectivity hollow fiber of this invention after carrying out gamma ray bridge formation of PVP which exists in a hollow fiber is shown. Drawing 4 shows holding the hollow filament configuration without dissolving the bridge formation PVP of transparence in DMAc, even after polysulfone is dissolved.
[0052] Drawing 5 is a transmission electron microscope photograph (40000 times) when observing the fiber structure of the hollow fiber of the opposite side (inside) of below-mentioned drawing 6 with an ultrathin section. It turns out that the PVP component (black) dyed from the male MIKKU acid concentrates and exists near the hollow filament internal surface so that clearly from drawing 5 .
[0053] Drawing 6 is a transmission electron microscope photograph (40000 times) when observing the fiber structure of a hollow fiber with an ultrathin section. Drawing 6 shows that the PVP component (black) dyed from the male MIKKU acid does not exist thin near the outside surface of a hollow fiber. In addition, a gray part is polysulfone.
[0054]
[Example] Hereafter, this invention is not limited by this although an example explains concretely.
[0055] Evaluation of the property of a hollow fiber was based on the following approaches.
1.5g of film by the [amount of effluents] artificial-kidney criteria <the eluting material test of permeable membrane> It put into water 150mL and the ultraviolet-rays absorbance in the wavelength of 220-350nm was measured by 10mm of layer length by considering as contrast the blank test liquid which carried out boiling cooling of the test fluid warmed at 70**5 degrees C for 1 hour beforehand. In addition, since an ultraviolet-rays absorbance (it only abbreviates to an absorbance hereafter) usually becomes the highest in 220nm, the following absorbances show the value in 220nm.

[DMAc insoluble matter] 1g of film dried at 120 degrees C for 5 hours After performing churning sufficient for 5 hours with DMAc50mL using the rotator, it ****(ed) with the glass filter (2G-2) which carried out weighing capacity beforehand, and the rate (% of the weight) to the film whole quantity of the amount of solid content obtained by drying for 8 hours at 130 degrees C was made into DMAc insoluble matter.
The amount of content PVP was converted from the amount of total nitrogen measured using the [amount of content PVP] elemental-analysis meter (made in the Yanamoto factory: CHN coder MT-5).
The amount with which DMAc insoluble matter is not filled among the amounts of [amount of bridge formation PVP] content PVP was made into the amount of bridge formation PVP.
This film after being immersed in DMAc and leaving a [distribution condition of bridge formation PVP] hollow fiber for 24 hours was observed with the optical microscope.
[0056] Moreover, after carrying out male MIKKU acid dyeing of the hollow fiber and considering as an ultrathin section, transparency mold electron microscope observation investigated the distributed condition of PVP.
After carrying out weighing capacity of the hollow fiber made into constant weight in the desiccator of [moisture absorption] phosphorus pentaoxide, weighing capacity of the hollow filament made into constant weight in 100% of humidity and a 25-degree C desiccator was carried out, and it computed as a percentage of the moisture to the amount of polymers.
Using 30 hollow filaments with a [permeability of hollow fiber] die length of 15cm, the small glass tube module was created and the permeability (water UFRS:ml/hr/mmHg/m2) of water in the differential pressure of the inside other than the film, i.e., the differential pressure between film, and about 100 mmHg(s) was computed.
[0057] Moreover, it is the cow plasma of total protein concentration 7.5 g/dl to this module 0.6 ml/min Circulating, it ****(ed) by differential pressure 50mmHg between film for 1 hour, the permeability (cow plasma UFRS:ml/hr/mmHg/m2) of cow plasma was measured from the average ******, and leak extent of albumin was investigated by the protein trial (ARUBUSU tex: made in [Sankyo Co., Ltd.] Miles) of ****.
[0058] About the still more nearly same module, they are solute water solutions, such as a myoglobin (molecular weight: 16,800 or 60 ppm), a pepsin (molecular weight: 35,000 or 300 ppm), and cow albumin (molecular weight: 67,000 or 300 ppm), 1.5 ml/min The transmission coefficient of each solute was computed by having made it circulate by the flow rate and having measured the solute concentration of permeate liquid.
[0059] Transmission coefficient = (permeate liquid concentration / supply liquid concentration) The film surface product which consists of 5,000-9,000 [modular permeability ability] hollow filaments is about 0.7 to 1.2m2. The permeability (physiological saline UFRP:ml/hr/mmHg) of the water in a physiological saline is measured using a module.
[0060] Next, it is bovine blood of 35 % of the weight of hematocrits, and protein concentration 4.5 g/dl 200 ml/min The highest permeability (plateau UFR:ml/min) of this module is measured circulating. Furthermore, the differential pressure between film is changed and the permeability (bovine blood UFCO:ml/hr/mmHg) in bovine blood is measured. The original blood at this time and the albumin concentration of **** are measured by the BCG method, and the permeability (%) of albumin is measured. If albumin is not penetrated substantially, it means that albumin permeability is 5% or less.
[0061] On the other hand, the dialysance of a urea (1000 ppm), a creatinine (200 ppm), a phosphoric acid (50 ppm), and vitamin B12 (20 ppm) is measured by the physiological saline system using the same module. For the flow rate by the side of blood, 200 ml/min and the amount of dialysing fluid side streams are 500 ml/min. Carrying out, ******** is 10 ml/min. It carried out.
[0062] - 37 degrees C also estimated the transparency engine performance the hollow fiber module.
[Endotoxin removal engine-performance] film area about 0.7m2 It is the liquid which produced the module and ****(ed) tap water from the outside of a hollow filament with about 0.3micro

filter to the inside 500 ml/min It supplies at a rate. The pressure loss at this time is measured, and the endotoxin concentration of supply liquid and permeate liquid is measured by the Limulus test method (Wako Pure Chem, Inc. make), and an endotoxin (it abbreviates to ET) elimination factor is computed.

[0063] K(ET) =(A-B) / Ax100 (%)

K(ET):ET elimination factor supply liquid ET concentration in formula: -- A permeate liquid ET concentration: -- the B example 1 polysulfone (P-3500:AMOCO shrine make) 18 section and the PVP(K-30: molecular weight 40,000 : BASF A.G. make) 9 section -- the DMAc43 section, the DMSO29 section, and the water 1 section -- in addition, keeping it warm at 80 degrees C, the churning dissolution was carried out for 15 hours, and the spinning undiluted solution was created. This spinning undiluted solution was clear at 25 degrees C at 58poise (drop viscosity: JIS-Z8803) homogeneity.

[0064] this spinning undiluted solution -- the annular slit of outer-diameter [of 0.35mm] phi, bore [of 0.25mm] phi, and 0.15mm of diameters phi of an injected hole -- a mouthpiece to 2.0 g/min comparatively -- coming out -- discharge and coincidence -- an injected hole to water -- 1.3 g/min It poured in at the rate. After it leads the die length of a dry type part to a 20-degree C coagulation bath (DMAc: water =20:80) by 300mm and it performs coagulation and rinsing, it permutes **** of a hollow filament by 70% of the weight of the glycerol water solution, and it is 33 m/min. It rolled round in the shape of skein at the winding rate.

[0065] the water UFRS of the obtained hollow filament -- 780 ml/hr/mmHg/m2 it was . the cow plasma UFRS -- 36 ml/hr/mmHg/m2 it is -- the protein trial of **** is - and leak was not accepted at all.

[0066] Furthermore, this hollow filament to film surface product 0.7m2 They are 25KG(ies) in the condition of having been filled up with water after producing the module and rinsing this module with 35-degree C warm water. Gamma irradiation was carried out with dosage. The absorbance of the extract from the hollow fiber of this module was 0.048.

[0067] After discharging the sealing liquid of this module furthermore, rinsing again, carrying out a seal to a polyethylene bag and giving packing for product modules, it is dosage 25KGy. Gamma irradiation sterilization was performed.

[0068] The physiological saline UFRP of the obtained module is the plateau UFR are 403 ml/hr/mmHg and according to bovine blood evaluation. 90 ml/min and bovine blood UFCO showed 50 ml/hr/mmHg and the high engine performance. Leak was not accepted substantially [the albumin permeability in **** at this time] at 0.21%. Moreover, the dialysance of this module is as follows and had penetrable high ability.

[0069]

尿素	クレアチニン	リン酸	VB12
170	147	142	93

Moreover, the PVP content of the hollow fiber taken out from this module was 5.8 % of the weight. Furthermore, though the absorbance of the extract from this hollow fiber was 0.046, moisture absorption showed 21.3 % of the weight and a high hydrophilic property.

the example 2 polysulfone (P-3500) 18 section and the PVP(K-30) 18 section -- the DMAc38 section, the DMSO25 section, and the water 1 section -- in addition, spinning was carried out like the example 1 using the spinning undiluted solution obtained by carrying out the churning dissolution for 15 hours, keeping it warm at 80 degrees C.

[0070] They are 25KG(ies) in the condition of having inserted the obtained hollow filament in the test tube, and having been filled up with water. Gamma irradiation was carried out with dosage. the water UFRS of the hollow filament after an exposure -- 360 ml/hr/mmHg/m2 it is -- the cow plasma UFRS -- 23 ml/hr/mmHg/m2 it was . The protein trial of **** at this time is **, and leak was hardly accepted. Moreover, although there were very many PVP contents in a hollow fiber as 8.7 % of the weight, the absorbance of the extract from this hollow filament had 0.093 and a high detergency.

the example 3 polyether-sulphone (VICTREX 4800P:ICI shrine make) 18 section and the PVP

(K-30) 9 section -- the DMSO72.6 section and the water 0.4 section -- in addition, keeping it warm at 80 degrees C, the churning dissolution was carried out for 6 hours, and the spinning undiluted solution was created. This spinning undiluted solution was clear at 25 degrees C at 104poise homogeneity.
[0071] Spinning was performed by making water into infusion like the example 1 using this spinning undiluted solution. the water UFRS of the obtained hollow filament -- 260 ml/hr/mmHg/m2 it was . the cow plasma UFRS -- 28 ml/hr/mmHg/m2 it is -- the protein trial of **** is - and leak was not accepted at all. Furthermore, they are 25KG(ies) in the condition of having inserted this hollow filament in the test tube, and having been filled up with water. Gamma irradiation was carried out with dosage. The absorbance of the extract from this gamma irradiation hollow fiber was 0.064. The DMAc insoluble matter of this film held the hydrophilic property with as good moisture absorption as 32.7 % of the weight 9% of the weight.
example 4 polysulfone (P-3500) -- the four sections -- the same -- polysulfone (P-1700:AMOCO shrine make) -- the 12 sections and the PVP(K-90: molecular weight 360,000 : BASF A.G. make) 6 section -- the DMAc47 section, the DMSO30 section, and the water 1 section -- in addition, keeping it warm at 80 degrees C, the churning dissolution was carried out for 15 hours, and the spinning undiluted solution was created. Spinning was carried out like the example 1 using the 64poise spinning undiluted solution at these 30 degrees C.
[0072] the water UFRS of the obtained hollow filament -- 180 ml/hr/mmHg/m2 it was . the cow plasma UFRS -- 26 ml/hr/mmHg/m2 it is -- the protein trial of **** is ** and leak was hardly accepted.
[0073] This hollow filament to film surface product 0.72m2 They are 25KG(ies) in the condition of having been filled up with water after producing the module and rinsing this module with 35-degree C warm water. Gamma irradiation was carried out with dosage.
[0074] The absorbance of the extract from the hollow fiber of this module was 0.047. Dosage 25KGy after discharging and re-rinsing the sealing liquid of this module furthermore Gamma irradiation sterilization was performed.
[0075] The physiological saline UFRP of the obtained module is the plateau UFR are 126 ml/hr/mmHg and according to bovine blood evaluation. 86 ml/min and bovine blood UFCO showed 43 ml/hr/mmHg and the high engine performance. Leak was not accepted substantially [the albumin permeability in **** at this time] at 0.26 % of the weight. Moreover, the dialysance of this module also showed the value high as follows.
[0076]

尿素	クレアチニン	リン酸	VB12
167	144	138	94

Moreover, the DMAc insoluble matter of the hollow fiber taken out from this module was 13.6 % of the weight, though moisture absorption also indicated the high hydrophilic property to be 21.3 % of the weight, 0.046 and the effluent level of the absorbance of the extract from this hollow fiber were low, and the absorbance of a modular sealing liquid had 0.115 and a high detergency.
example 5 polysulfone (P-3500) -- the 18 sections and the PVP(K-30) 9 section -- the DMAc44 section, the DMSO28 section, and the water 1 section -- in addition, the infusion presentation was set to DMAc/water =60/40 using the obtained spinning undiluted solution which carried out the churning dissolution for 15 hours, keeping it warm at 80 degrees C, and also spinning was carried out like the example 1. This hollow filament to a film surface product is 1.14m2. They are 25KG(ies) in the condition of having been filled up with water after producing and rinsing a module. Gamma irradiation was carried out with dosage. Dosage 25KGy after discharging and re-rinsing the sealing liquid of this module furthermore Gamma irradiation sterilization was performed.
[0077] The physiological saline UFRP of the obtained module is 955 ml/hr/mmHg/m2. Plateau UFR by bovine blood 106 ml/min and bovine blood UFCO showed 72 ml/hr/mmHg and the high engine performance. Leak was not accepted substantially [the albumin permeability in **** at this time] at 0.26%. Moreover, the value also with the high dialysance of this module was shown.

[0078]

尿素	クレアチニン	リン酸	VB12
190	175	172	125

0.037 and the effluent level of the absorbance of the extract from this hollow fiber were low, and the absorbance of a modular sealing liquid had 0.119 and a high detergency.
example 6 polysulfone (P-3500) -- the 15 sections and the PVP(K-30) 9 section -- the DMAc45 section, the DMSO30 section, and the water 1 section -- in addition, it dissolved and spinning of the obtained spinning undiluted solution was carried out like the example 1.
[0079] the water UFRS of the obtained hollow filament -- 950 ml/hr/mmHg/m2 it was . The protein trial of **** by cow plasma is -, and leak was not accepted at all.
[0080] Furthermore, this hollow filament to film surface product 0.67m2 They are 25KG(ies) in the condition of having been filled up with water after producing and rinsing a module. Gamma irradiation was carried out with dosage.
[0081] The absorbance of the extract from the hollow fiber of this module was 0.053. When ET removal engine performance of this module was furthermore evaluated, it is 0.67m2. In spite of a low film surface product, it is 500 ml/min. The pressure loss at the time of dipping was 98mmHg (s).
[0082] Moreover, the permeate liquid of 0.01 or less pg/dl of ET concentration could be obtained from the supply liquid of ET concentration 66 pg/dl, and the engine performance which was excellent as an ET filter was shown.
The hollow filament obtained in the example 7 example 6 is used, and it is 2 9cm of effective length, and 22cm of film surface products. The small module was created and the transmission coefficient of each solute was measured. Consequently, it turned out that the film with very sharp fractionation is obtained as shown in the following table.
[0083]
** Quality (molecular weight) Concentration (ppm) A transmission coefficient myoglobin (16,800) 60 0.956 A pepsin (35,000) 300 0.529 cow albumin (67,000) 300 The transmission coefficients of each solute when creating the same module as an example 7 and carrying out the same measurement using the PMMA (polymethylmethacrylate) hollow fiber of 0.111 marketing, were a myoglobin 0.77, a pepsin 0.23, and albumin 0.17, respectively.
The absorbance of the extract from the hollow fiber for which a bridge is not constructed [which was acquired in the one to example of comparison 6 examples 1-6] was what high values are indicated to be 0.265, 1.020, 0.316, 0.749, 0.271, and 0.493, respectively, and the PVP elution from the film is not stopped, and is a rejection and is not suitable for artificial-kidney criteria at the application as which a detergency is required.
[0084]
[Effect of the Invention] According to this invention, there is no concern of the effluent outflow from the film etc., the addition of a hydrophilic macromolecule which can give sufficient hydrophilic property to the film is possible, and, moreover, the hollow fiber of this invention can be used suitable for the membrane-separation field of others, such as medicine, the physic, food, etc. which need the outstanding **** engine performance and the outstanding detergency collectively.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] this drawing -- the extract from each hollow fiber of an example 6 and the example 6 of a comparison -- a spectrum -- the ultraviolet absorption spectrum measured by ****** UV-160 (Shimadzu make) is shown.
[Drawing 2] This drawing is a microphotography in which the underwater fiber configuration of the polysulfone system permselectivity hollow fiber of this invention containing bridge formation PVP is shown.
[Drawing 3] This drawing is a microphotography in which the fiber configuration in the inside of DMAc of the polysulfone system hollow fiber before carrying out gamma ray bridge formation of the content PVP is shown.
[Drawing 4] This drawing is a microphotography in which the fiber configuration of the hollow fiber which consists the polysulfone system permselectivity hollow fiber of this invention after carrying out gamma ray bridge formation of the content PVP of insoluble gamma ray bridge formation PVP when dissolving polysulfone in DMAc is shown.
[Drawing 5] This drawing is the transmission electron microscope photograph which observed the fiber structure of the internal surface of a hollow fiber with the ultrathin section.
[Drawing 6] This drawing is the transmission electron microscope photograph which observed the fiber structure of the outside surface of a hollow fiber with the ultrathin section.

[Translation done.]

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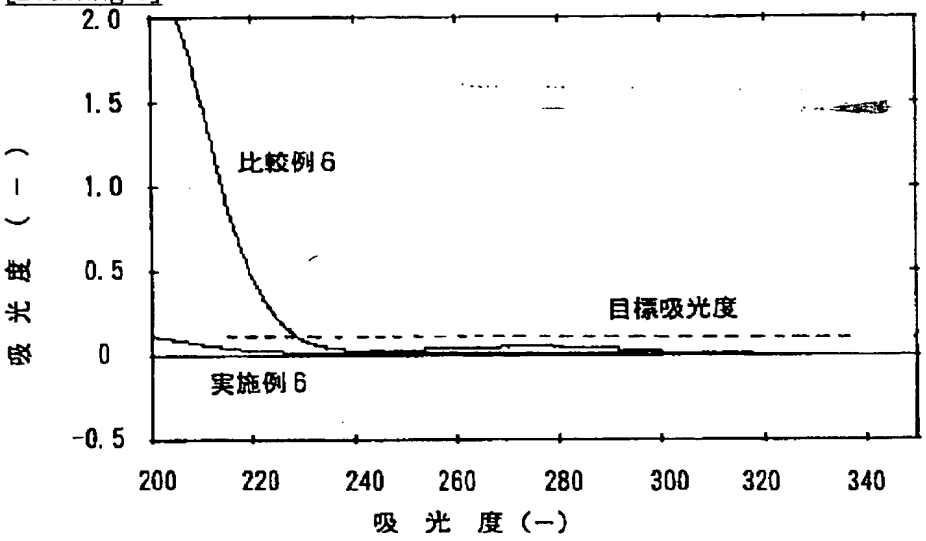
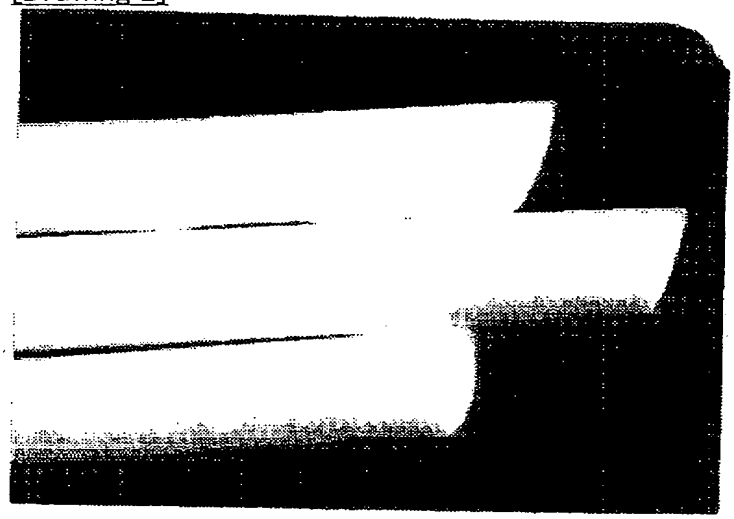
DRAWINGS

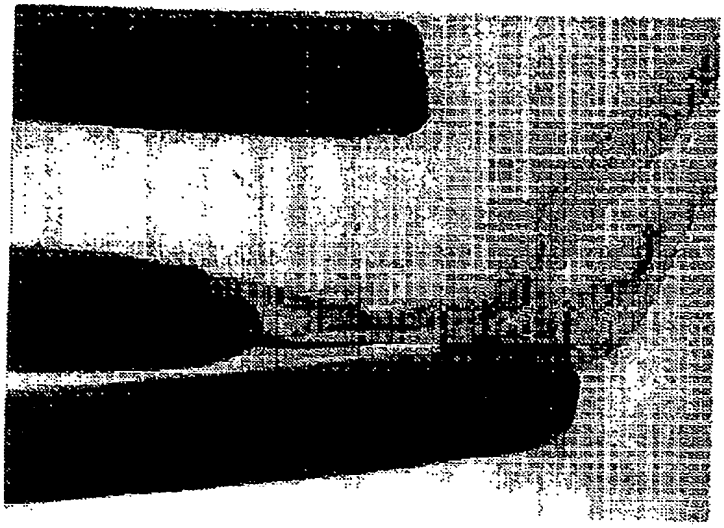
[Drawing 1]



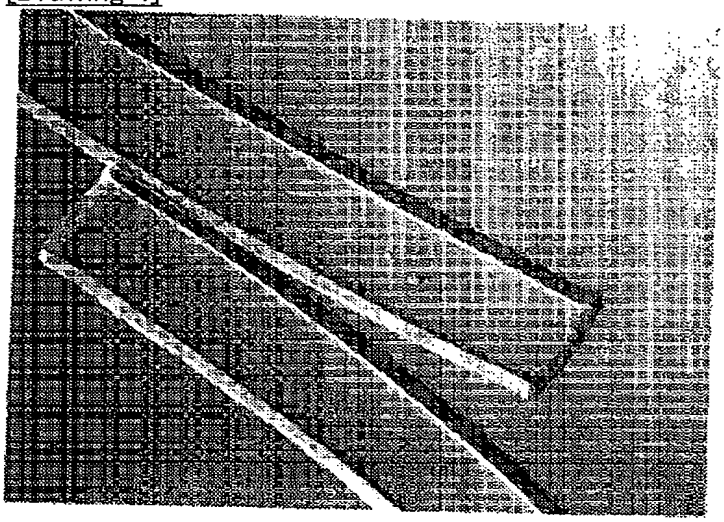
[Drawing 2]



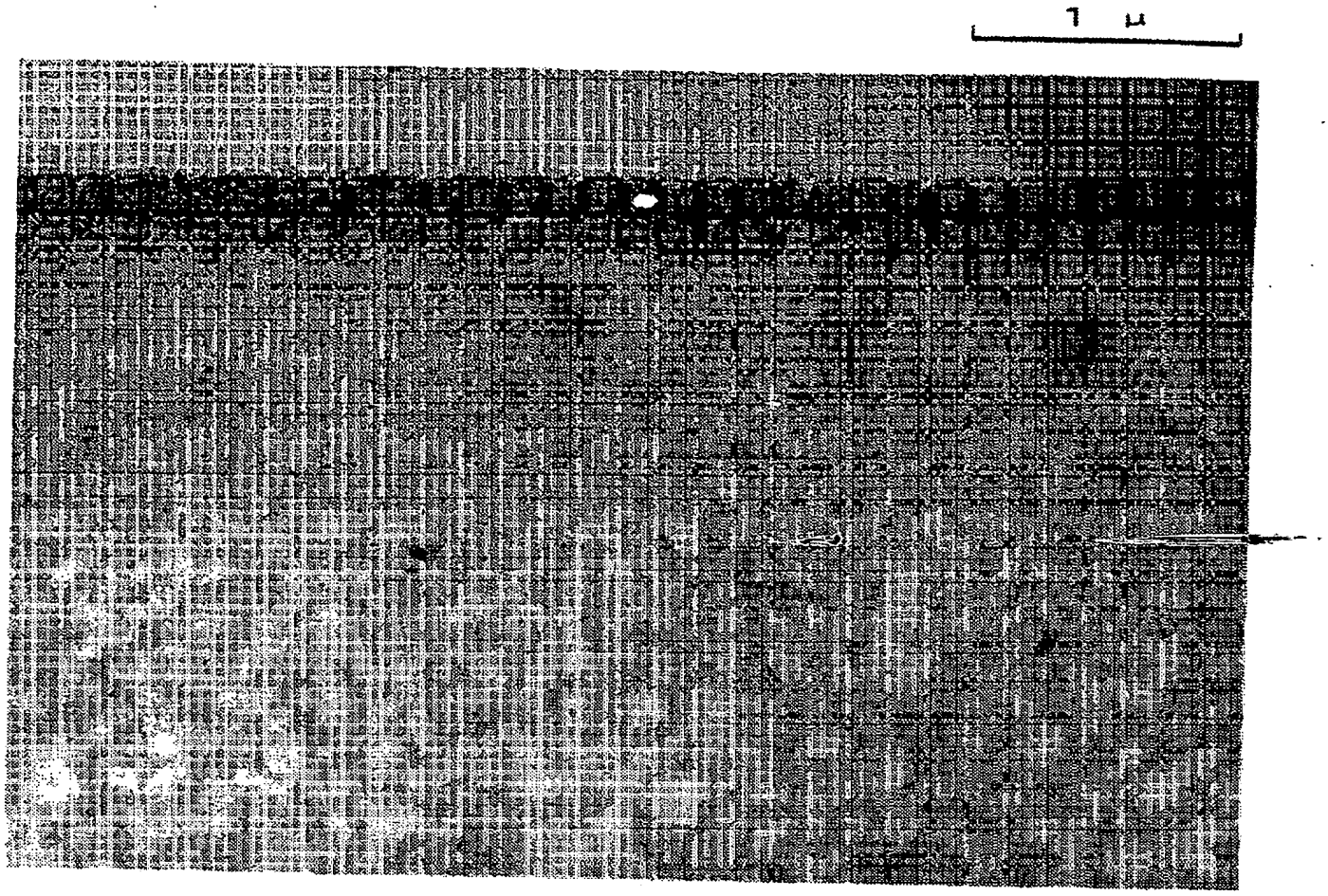
[Drawing 3]



[Drawing 4]

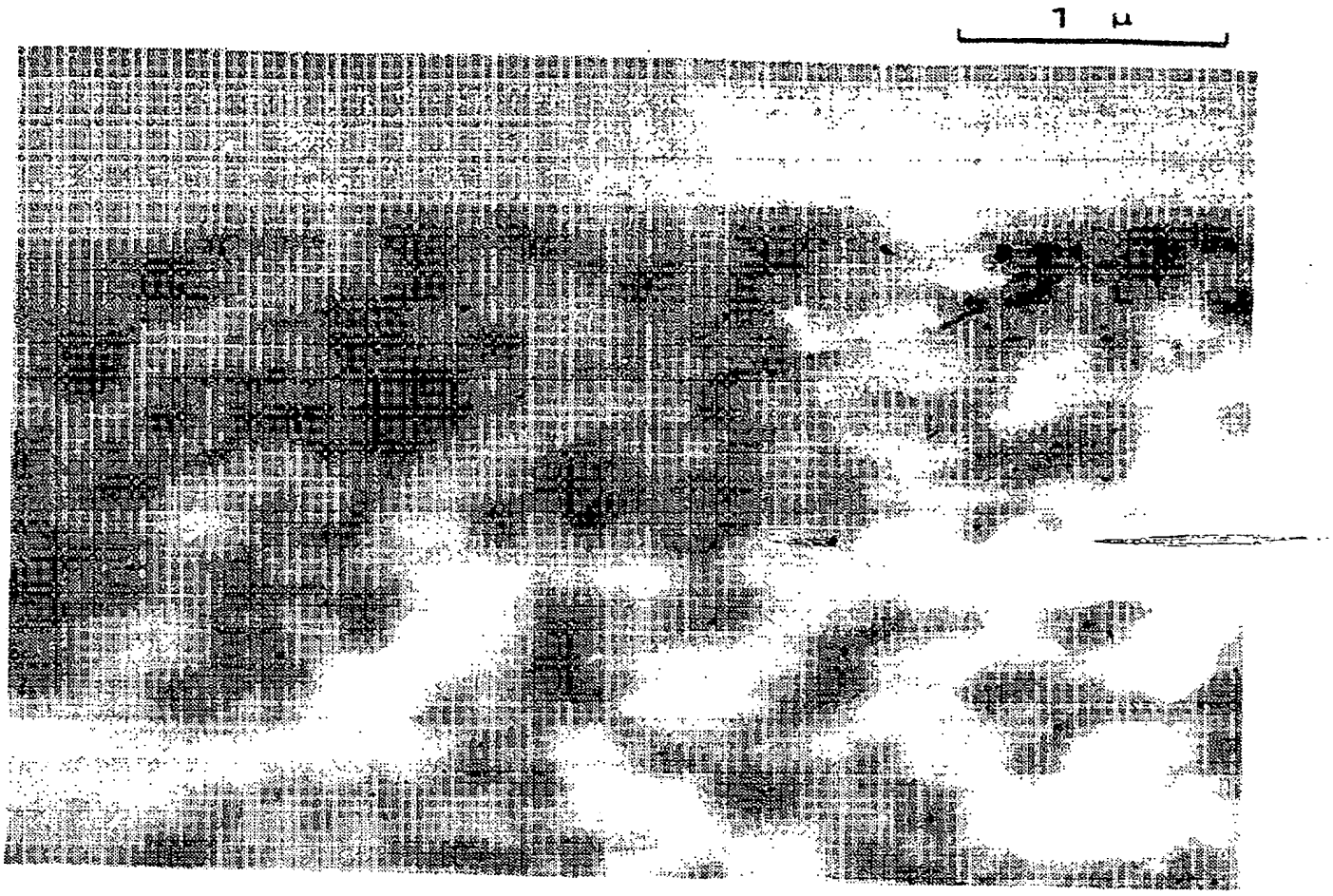


[Drawing 5]



[Drawing 6]

特許庁審査官 [illegible]



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